

California Environmental Protection Agency
Department of Pesticide Regulation
830 K Street
Sacramento, CA 95814

STUDY 178: PROTOCOL FOR MONITORING ACUTE AND CHRONIC
TOXICITY IN THE SACRAMENTO RIVER WATERSHED: WINTER 1998-99
November 23, 1998

I. INTRODUCTION

The Department of Pesticide Regulation (DPR) has a responsibility to ensure that pesticides are distributed and used in a safe manner. California law requires DPR to consider and encourage the use of pest control products and procedures that reduce human and environmental health hazards. DPR has developed a Pest Management Strategy to increase the adoption of reduced-risk pest management practices. The reduced-risk management practices involve economically viable techniques, that either currently exist or can be developed through research and education, that will lower the health and environmental risks of controlling pests. DPR is charged with evaluating the effectiveness of efforts to facilitate the adoption of these practices. One measure of success of this strategy would be decreasing incidences of pesticide related toxicity in the rivers and waterways of California.

The Sacramento River is the largest river in California both in flow and in drainage area (Figure 1). From Mount Shasta in the north to the Sacramento-San Joaquin Delta in the south, the river flows for 327 miles and drains approximately 27,000 square miles including agricultural, urban, and undeveloped land (Domalgalski and Brown, 1994). The Sacramento River provides 35% of the State's water supply, both drinking and agricultural, and is also an important resource for recreation and wildlife (Reynolds, et al., 1993). The primary source of water entering the system is surface runoff from the Sierra Nevada Mountains to the east and the Cascade Range to the north (CSLC, 1993). Runoff from rain events occurring in the Sacramento Valley provides significant short term increases in river flow. Seasonal rains occur from October to March with little significant rain from June to September. River flow during the summer is composed of dam releases of snow melt water for agricultural, recreational, and wildlife purposes.

In the Sacramento Valley, the organophosphorus insecticides diazinon and methidathion are the primary dormant season insecticides used on stone fruit and nut crops (DPR 1993; DPR 1994; DPR 1995). The dormant season application period coincides with the bulk of the seasonal rainfall, providing the potential for these pesticides to wash off target areas and into the Sacramento River. Pesticide use reports (DPR 1993-1995) indicate the majority of dormant spray insecticides are applied along the Feather River north of the Bear River and along the Sacramento River in northern Butte and Glenn Counties and southern Tehama County. The primary dormant spray OP insecticides, diazinon and methidathion, are applied in nearly identical areas (Figures 2 and 3) and these areas remain fairly stable from year to year. Runoff from orchard areas west of the Sacramento River chiefly flows into the Colusa Basin Drain which enters the Sacramento River at Knights Landing (Figure 4). Runoff from dormant spray areas east of the Sacramento River principally flows into Butte Creek, which has been engineered to drain into the Sutter Bypass via the Butte Slough. Runoff from the west side of the Feather River also drains into the Sutter Bypass. During periods of normal flow, the Sutter Bypass enters the Sacramento River via the Sacramento Slough at Karnak. During periods of high flow, the Sutter Bypass channel fills completely with runoff from this area plus water diverted from the Sacramento River. This flow merges with the Feather River eight miles prior to entering the Sacramento River, forming a two mile wide channel which inundates the Sacramento Slough. During floods, a large portion of the flows for the Sacramento River and the Sutter Bypass/Feather River will be diverted into the Yolo Bypass. Runoff from areas east of the Feather River drain into the Feather River above Nicolaus.

A one year DPR study and a three year U.S. Geological Survey (USGS) study of the Sacramento River have shown that most diazinon and methidathion detections were observed during the dormant spray season (MacCoy et. al. 1995; Ganapathy et. al. 1998). No other organophosphate (OP) or carbamate (CB) insecticides, analyzed in those studies, were detected. Atrazine and simazine have also been detected during winter monitoring by the USGS. These detections occurred almost exclusively in conjunction with rain events indicating that rain runoff was the primary source of pesticides entering the rivers. Toxicity has been found at Gilsizer Slough, which drains some of the area west of the Feather River and flows into the Sutter Bypass. *Ceriodaphnia dubia* acute mortality was 100% in five of the seven consecutive weekly samples. This toxicity appeared related to levels of pesticides detected in four of the samples with an indeterminate cause of toxicity in the fifth sample (Foe and Sheipline, 1993).

During the winter of 1996-97 DPR conducted toxicity monitoring at sites along the Sacramento River and Sutter Bypass (Nordmark et. al. 1998a). Extensive flooding occurred in January, 1997 which greatly affected river discharges and modified the sampling schedule. No chronic toxicity or reproductive impairment was found at the Sacramento River at Bryte site and no acute toxicity was found at the Sutter Bypass site. A single diazinon pulse lasting up to eight days was detected in the Sacramento River in late-January and diazinon was also detected in the Sutter Bypass at this time. Methidathion was detected in a single sample from the Sacramento River and from the Sutter Bypass. These detections appeared rain event related. Diazinon was detected in a second pulse lasting up to two weeks in late-February in the Sutter Bypass, but did not appear to be related to any storm event.

The winter of 1997-98 was again wetter than normal. No chronic toxicity or reproductive impairment was found at the Sacramento River at Alamar Marina site and no acute toxicity was found at the Sutter Bypass site (Nordmark 1998b). DPR detected diazinon in 40% of the Sacramento River samples, with the highest level reported at 0.17 µg/L, and in 30% of the Sutter Bypass samples, with a maximum concentration of 0.088 µg/L. DPR added a chemical analysis screen for nine soil applied herbicides to the tests performed at each site during 1997-98. Diuron and simazine were detected at both the Sacramento River and Sutter Bypass sites while bromacil was detected only at the Sutter Bypass site.

This study is the third year of a five-year effort to monitor dormant spray runoff in the Sacramento River watershed. In this study we will continue to look at acute toxicity to *C. dubia* in a small watershed where the discharging waters do not contain major inputs from municipal or industrial sources. We will also investigate the potential for chronic toxicity in a section of the Sacramento River downstream of major dormant spray insecticide inputs in the watershed. Selected herbicides will also be monitored as recommended in the memo: (Goh, 1997) "Category and recommendation of currently registered pesticides for surface water monitoring during FY97-98." Long-term monitoring of acute and chronic toxicity will help scientists at DPR evaluate the effectiveness of programs designed to decrease the runoff of dormant spray insecticides and selected herbicides.

II. OBJECTIVES

The objective of this study is to monitor the occurrence of acute and chronic toxicity in the Sacramento River watershed during the dormant spray season. Additionally,

levels of specific organophosphate and carbamate insecticides and selected herbicides which have a potential to enter the Sacramento River with surface runoff will be monitored. A companion study will be conducted to monitor pesticide levels and toxicity in the San Joaquin River.

III. PERSONNEL

This project will be conducted by the Environmental Hazards Assessment Program (EHAP) under the general direction of Don Weaver, Ph.D., Senior Environmental Research Scientist (Supervisor). Key personnel are listed below:

Project Leader: Craig Nordmark

Field Coordinator: Andy Fecko

Senior Scientist: Lisa Ross, Ph.D.

Study Design/Data Analysis: Terrell Barry, Ph.D.

Toxicity Tests: Charlie Huang, Ph.D., California Dept. of Fish and Game

Chemist: Jane White, Jorge Hernandez, Duc Tran, California Dept. of Food and Agriculture

Agency and Public Contact: Kevin Bennett

Questions concerning this project should be directed to Kevin Bennett at: (916) 324-4100 Fax: (916) 324-4088

IV. STUDY PLAN

Sampling for acute toxicity will be conducted from a new site, the South Butte Road Bridge across the Wadsworth Canal. This site replaces the Sutter Bypass site used in previous years. Two years of high flows in the Sutter Bypass were composed largely of Sacramento River water entering the via the Tisdale Weir. At very high flows the Sutter Bypass does not truly represent a small watershed, which is our intent when sampling for acute toxicity. The Wadsworth Canal site receives predominantly agricultural water from a small watershed, it avoids the backflow from the Sutter Bypass when bypass levels are high, and it discharges into the Sutter Bypass just above the Sutter National Wildlife Refuge (Figure 4). We will continue to do a chemical analysis of samples from a bridge across the east channel of the Sutter Bypass at the Karnak pumping station, or from the levee at Kirkville Road in the event of flooding at Karnak, for continuity purposes. Sampling for chronic toxicity will be conducted on the Sacramento River from the Alamar Marina dock as this site receives discharge from all the major agricultural tributaries (Figure 4) but is above the discharge of the largely non-agricultural American River and the urban runoff of the City of Sacramento. Discharge records are available for both the Wadsworth

Canal, Karnak, and Alamar sites from nearby gauging stations. This information will be used to correlate any changes in chemical concentrations to fluctuations in flow and may be useful for modeling efforts should they be undertaken.

Monitoring will commence prior to the onset of the dormant spray season (early December 1998) and continue through the second week of March 1999. Background samples will be collected for one week, beginning prior to dormant spray applications, then monitoring will resume once applications have begun and continue until no later than March 19, 1999. Additional data collection will include *in-situ* measurements of water pH and temperature, dissolved oxygen, and specific conductance.

V. SAMPLING METHODS

Acute toxicity sampling will be conducted twice per week at Wadsworth Canal at South Butte Road. We will continue to collect samples at Karnak twice per week for chemical analysis only. Sampling for chronic toxicity will be conducted weekly on the Sacramento River at Alamar. One chronic sample constitutes the collection of samples on days zero, two and four of each week (e.g. Monday, Wednesday and Friday). Water collected on those days will be delivered the following day to the California Department of Fish and Game-Aquatic Toxicology Laboratory (CDFG-ATL) for testing and sample renewal. Chemical analysis will be performed on each sample collected for both acute and chronic tests. Selected OP and CB pesticides will be analyzed in three analyses. Selected herbicides will also be analyzed in a fourth analysis (Table 1). The herbicides are not expected to reach levels where they would contribute to *C. dubia* toxicity, but will be monitored to look for possible effects on other aquatic life (Table 2).

At each sampling site, water will be collected from as close to center channel as possible using a depth-integrating sampler (D-77) with a 3-liter Teflon® bottle and nozzle. As river levels rise, the Karnak site is flooded by water from the Sacramento and Feather Rivers. In that case, samples will be drawn at Kirkville Road, approximately 10 miles upstream. Sampling at the Kirkville Road site will be done by wading into the stream with a grab pole consisting of a new glass bottle at the end of a three meter pole. Surface water subsamples will be composited temporarily in a stainless steel container until the appropriate volume of water has been collected. The composited sample will be stored on wet ice until delivered to the processing facility at West Sacramento. Immediately upon arrival at the processing facility, the

composite sample will be split into 1-liter amber glass bottles, using a Geotech® 10-port splitter, then sealed with Teflon®-lined caps. The organophosphate and carbamate chemical analysis samples will be preserved by acidification with 3N hydrochloric acid to a pH between 3.0 to 3.5. At this pH, most OP and CB pesticides are sufficiently preserved with the exception of diazinon. Therefore, diazinon and the herbicides will be analyzed from separate, unacidified, split samples. Samples submitted for toxicity tests will not be acidified. Sufficient water will be collected at each sampling event to provide approximately four liters for chemical analysis, two liters for toxicity testing, and any additional water required for quality control (QC) and backup samples.

Split samples for chemical analysis will be transported on wet ice to the California Department of Food and Agriculture (CDFA) Center for Analytical Chemistry within three days of collection. Split samples for toxicity testing will be delivered on wet ice to the CDFG-ATL within 24 hours of collection. CDFG will measure and record other parameters of the split samples including totals of ammonia, alkalinity, hardness, and specific conductivity as part of their toxicity testing.

VI. TOXICITY TESTING AND CHEMICAL ANALYSIS

Toxicity testing conducted by the CDFG-ATL will follow current USEPA procedures using the cladoceran *Ceriodaphnia dubia* (U.S. EPA, 1993). The CDFG-ATL has been accredited by the California Department of Health Services' Laboratory Accreditation Program. Acute toxicity will be determined using a 96-hour, static renewal bioassay in undiluted sample water. Chronic toxicity will be determined using a 7-day bioassay of undiluted sample water with *C. dubia* and will follow current USEPA guidelines (U.S. EPA, 1994). For example, test organisms used in chronic testing will be subjected to sample water collected day zero on the following day (day 1). Sample water collected on days two and four will then replace test water on days three and five, respectively. All bioassays must commence within 36 hours of sample collection. Data will be reported to the project leader as percent survival on each day for the duration of the tests.

Chemical analysis will be performed by the CDFA-Center for Analytical Chemistry. The reporting limit will be the lowest concentrations of analyte that the method can detect reliably in a matrix blank (DPR, 1996). The reporting limits for this study are listed in Table 1. Chemical analytical methods will be provided in the final report. The total number of samples is presented below.

Number of Toxicity Tests

2 acute tests/week x 11 weeks of study	22
1 chronic test per week x 11 weeks of study	<u>11</u>
Total number of toxicity tests	<u>33</u>

Number of Chemical Analyses

8 (OP, CB, diazinon and herbicides) per acute toxicity sample: 8 analyses x 2 acute toxicity sampling events/week x 11 weeks	176
4 (OP, CB, diazinon and herbicides) per chronic toxicity sampling event: 4 analyses x 3 chronic sampling events (=1 chronic sample)/week x 11 weeks	<u>132</u>
Subtotal	<u>308</u>

Quality Control

Continuing QC (approx. 10% of total chemical analyses)	<u>30</u>
Total number of chemical analysis samples	<u>338</u>

VII. QUALITY ASSURANCE/QUALITY CONTROL

Chemical Analysis

Quality control will be conducted in accordance with Standard Operating Procedure QAQC001.00. Ten percent of the total number of primary analyses will be submitted with field samples as rinse blanks, matrix blanks, and blind matrix spikes.

VII. DATA ANALYSIS

Toxicity data will be used to establish baseline information on the occurrence of acute and chronic events at these sites. A correlation matrix will be established to identify potential relationships between measured environmental parameters, discharge, toxic events, and chemical concentrations. Further analysis may include multivariate analysis, depending on preliminary analysis results.

IX. TIMETABLE

Site Survey and Selection	September 1998
Field Sampling	December 7 through 11, 1998 and January 4 through March 12, 1999
Preliminary Report	Aug. 1999

X. REFERENCES

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- Mayer, F.L. and M.R. Ellersieck. 1986. Manual of Acute Toxicity: Interpretation and Data Base for 410 Chemicals and 66 Species of Freshwater Animals. U.S. Fish and Wildlife Service, Washington, DC.
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- U.S. Environmental Protection Agency. Draft. Pesticide Ecological Effects Database. For information contact: Brian Montague, Ecological Effects Branch, Environmental Fate and Effects Division (H7507C), U. S. Environmental Protection Agency, 401 M St. S.W., Washington, D.C., 20460.
- U.S. Environmental Protection Agency. 1993. Methods for measuring the acute toxicity of effluents and receiving waters to freshwater and marine organisms. 4th ed. EPA/600/4-90/027F. August 1993.
- U.S. Environmental Protection Agency. 1994. Short-term methods for estimating the chronic toxicity of effluents and receiving waters to freshwater organisms. 3rd ed. EPA-600-4-91-002. July 1994.

Table 1. California Department of Food and Agriculture, Center for Analytical Chemistry organophosphate and carbamate insecticide and triazine herbicide screens for the Sacramento River toxicity monitoring study.

Organophosphate Pesticides in Surface Water by GC		N-Methyl Carbamate in Surface Water by HPLC		Herbicides in Surface Water by HPLC	
Method: GC/FPD		Method: HPLC/Post Column-fluorescence		Method: HPLC/Post Column-fluorescence	
Compound	Reporting Limit (µg/L)	Compound	Reporting Limit (µg/L)	Compound	Reporting Limit (µg/L)
Chlorpyrifos	0.04	Carbaryl	0.05	Atrazine	0.05
Diazinon ¹	0.04	Carbofuran	0.05	Bromacil	0.05
Dimethoate (Cygon)	0.05			Diuron	0.05
Fonofos	0.05			Cyanazine	0.2
Malathion	0.05			Hexazinone	0.2
Methidathion	0.05			Metribuzin	0.2
Methyl parathion	0.05			Prometon	0.05
Phosmet	0.05			Prometryn	0.05
				Simazine	0.05

¹ Diazinon is analyzed from a separate, unpreserved, split sample. Other OP and CB chemical samples are preserved with 3N HCl to a pH of 3-3.5 to retard analyte degradation. See text.

Table 2. Relative acute 96-hour LC50 of pesticides in the insecticide and triazine herbicide screen. This table is for reference only and does not represent an exhaustive search of the literature. All concentrations are in mg/L (ppm).

Insecticides	Organism						
	<i>Ceriodaphnia dubia</i>	<i>Daphnia magna</i>	<i>Daphnia pulex</i>	<i>Pteronarcys californica</i>	Rainbow Trout	Fathead Minnow	Bluegill
Carbaryl	0.012e	0.0056b	0.0064b	0.0048b	1.3a	1.4e	8.2b
Carbofuran		0.039d	(0.015)a		22-29a	0.87-1.9b	1.75a
Chlorpyrifos	0.00008e	0.00021c	(0.017)a	0.01b	0.003a	0.055e	0.003b
Diazinon	0.0005e	0.0012e	0.0008b	0.025b	2.6-3.2a	7.8d	16a
Dimethoate		2.5c		0.043b	6.2a		6a
Fonofos	.00026e	0.002c	(1)a		0.05a	1.09e	0.028a
Malathion		0.001b	0.0018b	0.01b	0.007-0.23b	0.086-0.11b	0.1a
Methidathion	0.002e	0.003c			0.01a	8.9d	0.002a
Methyl parathion		0.0048c	(0.0073)a		2.7a	8.9b	4.4b
Phosmet		0.0056-0.011c	(0.085)a		0.23a	7.3d	0.07a
Herbicides							
Atrazine		49c	(6.9)a		8.8a	15d	16a
Bromacil		121d	(119)a		75a		71a
Cyanazine		49c	(42-106)a		9b	18b	20b
Diuron	12.1e	8c	1.4b	1.2b	5.6a	14.2d	5.9a
Hexazinone		152c			320-420a	274a	370-420a
Metribuzin		0.042b	(4.5-35)a		64a		80a
Prometon		59.8d			12a		40a
Prometryn		18.9c	(12.66)a		2.5a		10.0a
Simazine		1c	(>100)a	1.9b	>100a	>10b	90a

NOTES:

Numbers in italics are for 48 hour tests, all others are 96 hour tests.

Numbers in parenthesis are for Daphnids where the species was not indicated.

Bold numbers are reported as EC50 for 48 hour tests.

SOURCES:

- The Pesticide Manual, Tenth Edition
- Manual of Acute Toxicity, U.S. Fish and Wildlife Service
- Department of Pesticide Regulation Aquatic and Wildlife Toxicity compilation.
- Draft Pesticide Ecological Effects Database, U.S. EPA
- Background Information on 9 Selected Pesticides, CVRWQCB

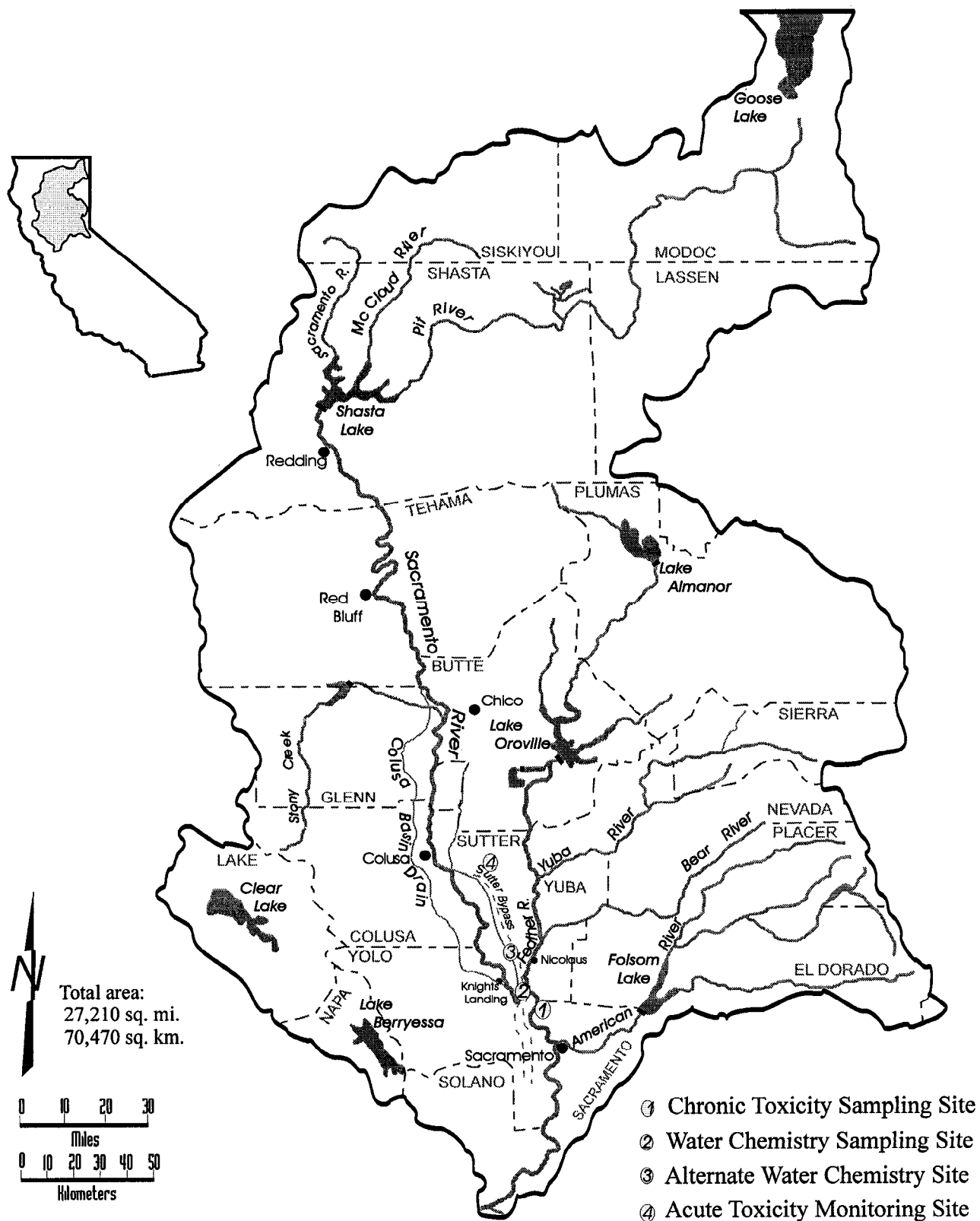


Figure 1. Map of the Sacramento River Hydrologic Basin.

Figure 2. Average diazinon use per section in the Sacramento River Watershed during January and February, 1992-95.

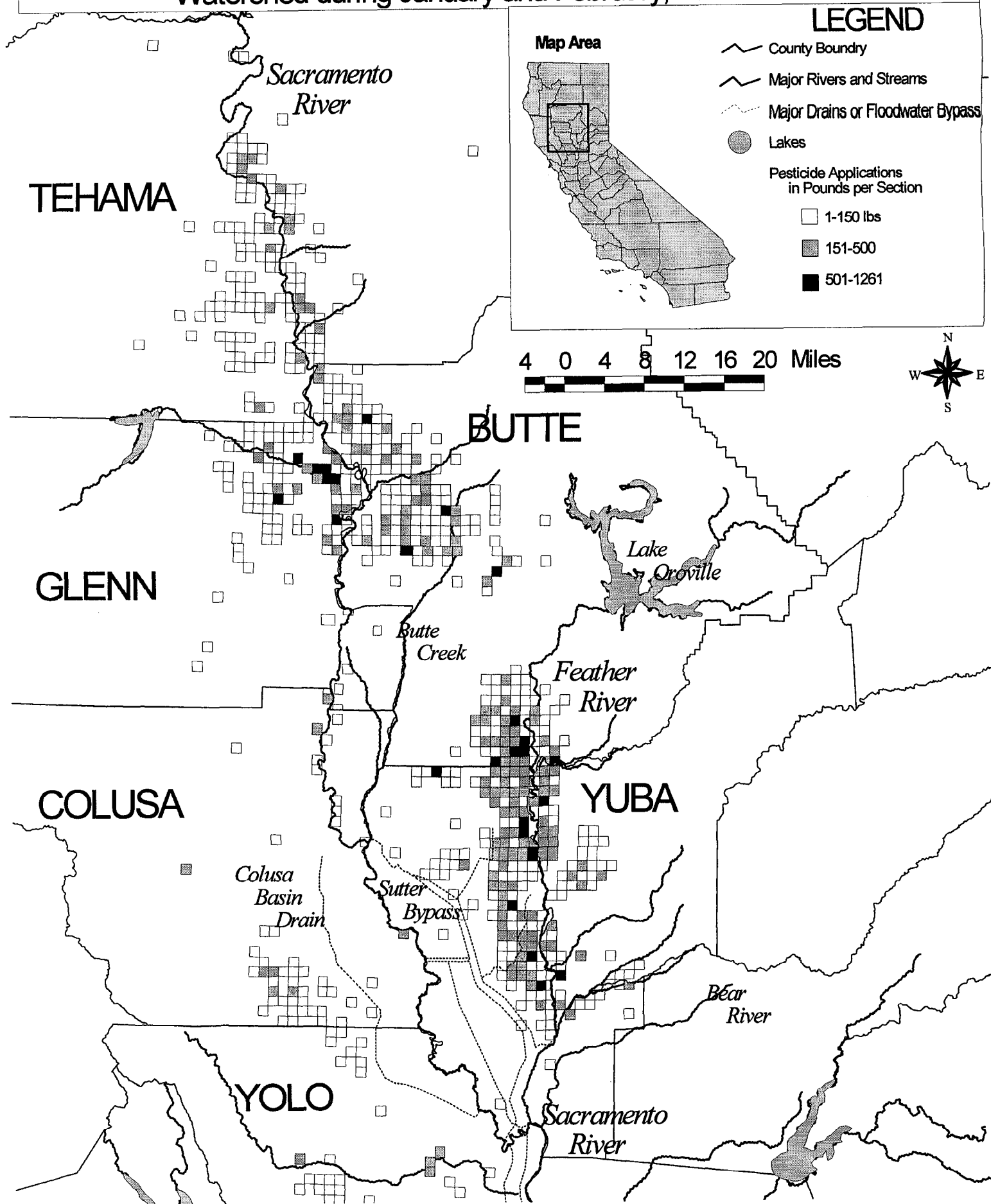
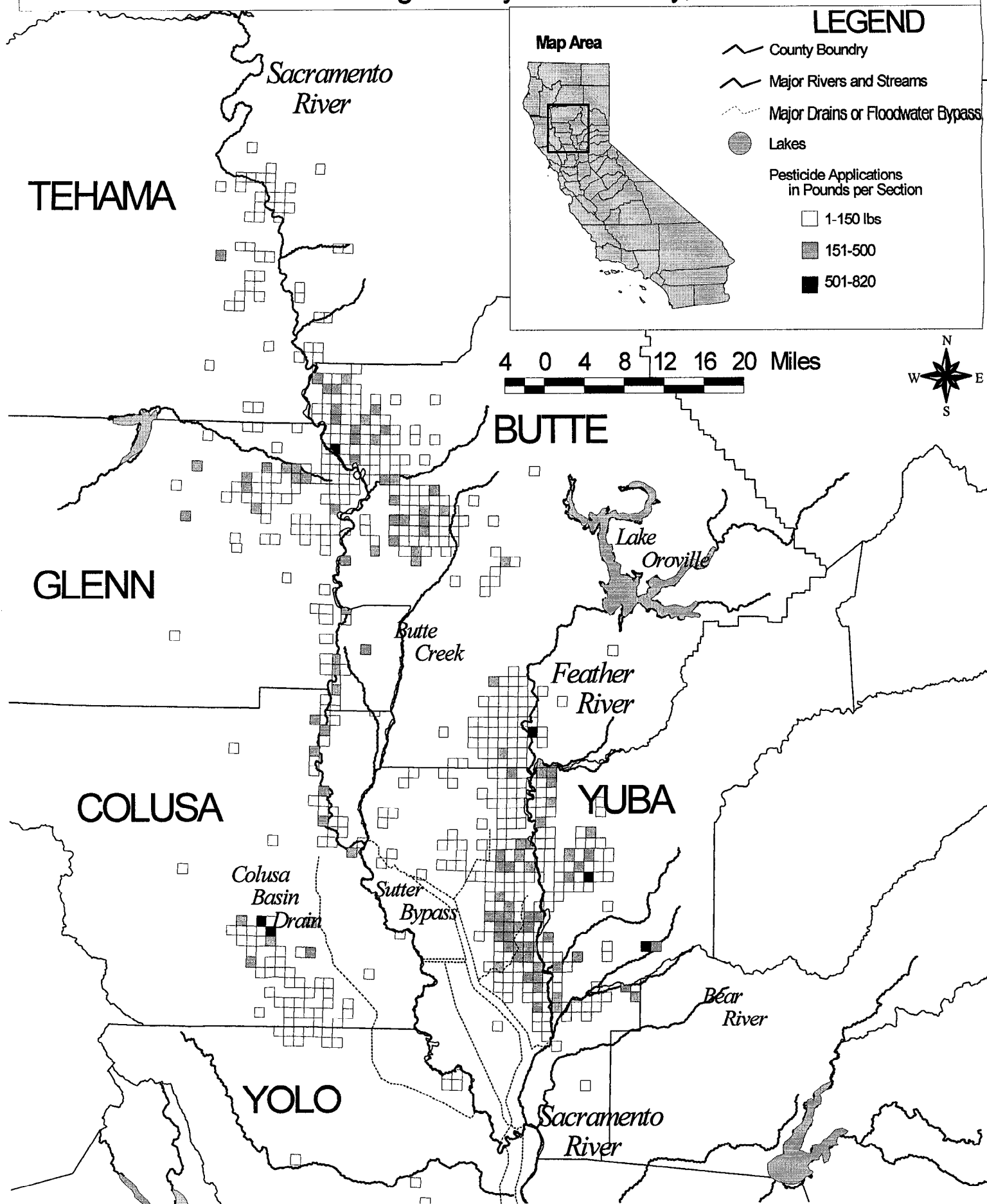


Figure 3. Average methidathion use per section in the Sacramento River Watershed during January and February, 1992-95.



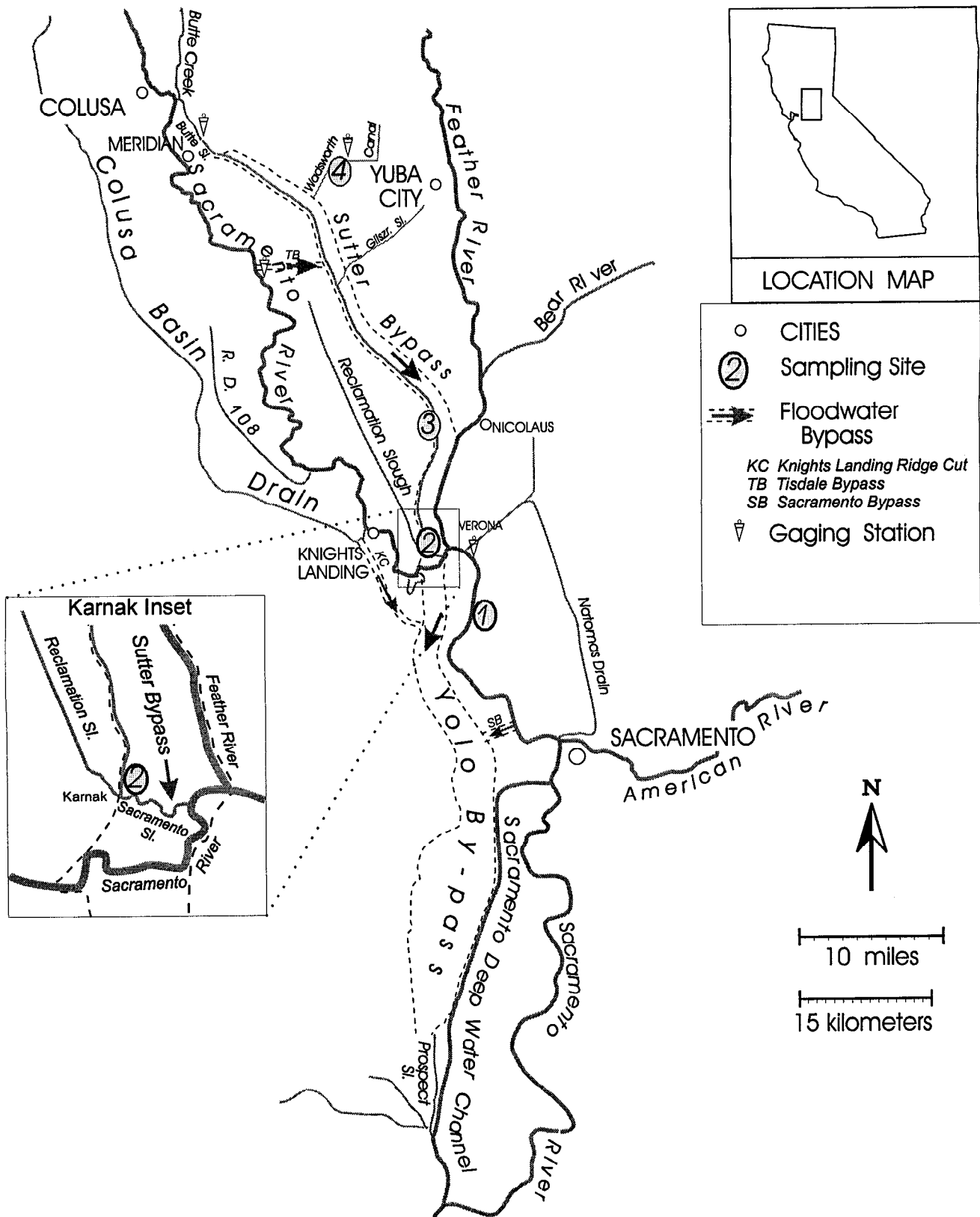


Figure 4: Sampling sites in the Sacramento River watershed.
 Site 1 = Alamar Marina, Sacramento River Chronic Toxicity Site.
 Site 2 = Sutter Bypass at Karnak Pumping Station, Water Chemistry Site.
 Site 3 = Sutter Bypass at Kirkville Road, Alternate Water Chemistry Site.
 Site 4 = Wadsworth Canal, Acute Toxicity Monitoring Site.